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(54) Title: TOBACCO TREATMENT

(57) Abstract: The invention relates to a method of treating tobacco to reduce or eliminate nitrosamines therefrom. The method comprises the use of a supercritical fluid extraction medium at elevated temperature and pressure to selectively remove nitrosamines compared with nicotine removal. The nitrosamine content for all tobacco types can be reduced.

### Tobacco Treatment

The present invention relates to a method of treating tobacco to reduce or eliminate the content of nitrosamines therein, particularly tobacco specific nitrosamines.

Tobacco specific nitrosamines include N'-nitrosonornicotine, 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone, N'-nitrosoanatabine and N'-nitrosoanabasine.

Various methods are known for the removal of nitrosamines from tobacco. In US 5,803,081 and WO 98/58555 green leaf tobacco (i.e. tobacco prior to curing) is subjected to microwave radiation, convection heating or freeze drying in order to kill microbes thought to be responsible for the production of nitrosamines during curing of the tobacco. A disadvantage of this method is that the method includes the requirement of specific curing practices for the tobacco, which curing practices are carried out on the tobacco at an early stage post-harvest.

An aim of the present invention is to provide an improved method for reducing nitrosamines in tobacco.

A further aim of the present invention is to provide an improved method for selectively reducing nitrosamines in tobacco.

The present invention provides a tobacco treatment process wherein tobacco is subjected to treatment with a

supercritical fluid extraction medium to extract nitrosamines from said tobacco.

Preferably, nitrosamines are separated from the supercritical fluid extraction medium by subjecting the extraction medium to a nitrosamine removal process.

Suitably, the nitrosamine removal process may comprise a chemisorption step. Preferably, the chemisorption step may comprise the use of an ion exchanger.

Alternatively, the nitrosamine removal process may comprise an adsorbent step. A suitable adsorbent may be selected from one or more of the group consisting of glass beads, activated charcoal, aluminium silicate and zeolites. Other suitable adsorbents known to those persons skilled in the art may also be used.

In a further alternative, the nitrosamine removal process may comprise treatment of the extraction medium with ultraviolet (UV) light, resulting in the breakdown of nitrosamines in the extraction medium.

Yet further alternatives include the removal of nitrosamines by precipitating the nitrosamines from the extraction medium; by subjecting the extraction medium to nitrosamine specific enzyme breakdown; or by chromatographic or other methods of separation known to those persons skilled in the art.

The process for nitrosamine removal from the extraction medium may comprise more than one of the above outlined nitrosamine removal processes. In certain circumstances, at least, use of a plurality of removal processes (together comprising a multi-process) will result in an enhanced specificity of removal of nitrosamines. For example, the nitrosamine removal process may be a multi-process comprising a chemisorption step in combination with or followed by treatment with UV light. Prior to the UV light treatment a washing step may be required to remove the nitrosamines from the chemisorption medium, the UV light then being applied to the washings. Water, an acid, a salt solution or an alcohol may suitably be used in the washing step.

Suitably, the extraction medium having had some, if not all, of the nitrosamines removed therefrom may be brought into contact with tobacco, such that extract(s) other than nitrosamines in the medium may be incorporated or re-incorporated with the tobacco. Such extract(s) may, for example, comprise nicotine and/or flavour substances.

Much by preference, the supercritical fluid used is supercritical carbon dioxide, although other supercritical fluids known to the skilled person may be suitable.

Suitably, an acid, preferably an organic acid, may be added to the tobacco prior to treatment of the tobacco with supercritical fluid. Alternatively, the acid may be

incorporated with the supercritical fluid. Furthermore, when an ion exchanger or adsorbent material is present, the acid may be incorporated with the ion exchanger or adsorbent. A suitable acid may be an organic acid selected from one or more of the group consisting of malonic acid, ascorbic acid, succinic acid, glutaric acid, adipic acid, malic acid, tartaric acid, mucic acid and citric acid, or a salt derivative(s) thereof. Preferably, the organic acid is a citric acid salt, potassium citrate for example. Other suitable acids may be mineral acids, for example sulphuric acid and phosphoric acid. Suitably, when the acid is applied to the tobacco the acid is in solution. Such solution may be applied by spraying. Advantageously, the application of the acid to the tobacco may take place in a casing cylinder conventionally used within the tobacco industry for applying casings to tobacco.

Other modifiers, such as organic solvents or alcohols, for example, may alternatively or additionally be used.

Preferably, the extraction treatment of the tobacco with the supercritical fluid takes place at an elevated pressure and temperature. Suitably, when the supercritical fluid is carbon dioxide a pressure in the range of 100 to 350 bar may be used, preferably the pressure being about 200 to 300 bar and more preferably being about 240 to 260 bar. Preferably, the temperature used is greater than about 35° Celsius, more

preferably in a range of about 35 to about 140° Celsius, and even more preferably in a range of about 35 to about 90° Celsius.

Advantageously, the tobacco is placed in a closable chamber or bomb during the extraction treatment thereof with the supercritical fluid.

Heating may be effected by heat transfer or by electromagnetic radiation (i.e. microwave or radiofrequency heating). When electromagnetic radiation is used the closed chamber or bomb will, of course, have to be made of a non-electromagnetic absorbing material, e.g. non-metallic material, capable of withstanding the operating pressure. A suitable such material may be comprised of a polyfluorohydrocarbon material, such as Teflon (Trademark) for instance.

The technical effect of removing tobacco specific nitrosamines by processing of tobacco with supercritical fluid was heretofore unknown. Much by preference the conditions at which the extraction treatment of the tobacco with the supercritical fluid takes place are biased towards extraction in the supercritical fluid of nitrosamines, as compared with other tobacco specific compounds, such as nicotine for instance. Advantageously, no or very little, nicotine is removed from the tobacco in the extraction medium. Conditions which favour nitrosamine extraction (compared with nicotine

extraction) include a pH of the tobacco of less than about 6.5, and preferably less than about 5.5.

Preferably, the ratio of the percentage reduction in nitrosamines to the percentage reduction in nicotine in tobacco, which tobacco has been subjected to the process of the present invention, is in the range of about 1.1:1 to about 18:1, more preferably about 1.3:1 to about 10:1, and even more preferably about 2:1 to about 6:1.

For a given set of treatment conditions, including, for example, the mass flow rate of the extraction medium per unit mass of the tobacco, there will occur, after the elapse of a time interval from commencement of the treatment process, a maximum difference between the extraction of the (greater) percentage amount of nitrosamines and the (lesser) percentage amount of nicotine. Thus it may be preferable to discontinue the extraction treatment at or about this time.

A suitable mass flow rate of the supercritical fluid extraction medium per kg of tobacco is in the range of about 1kg/h to about 55kg/h, and is dependent on the process conditions, such as the tobacco packing density in the chamber and the size of the chamber. Advantageously the mass flow rate of the supercritical fluid extraction medium per kg of tobacco is in the range of 10 to 40kg/h, more advantageously is in the range of 15 to 35kg/h and is even more

advantageously about 30kg/h, although these figures do depend on what the desired product characteristics are.

Advantageously, the tobacco treated in accordance with the process of the present invention is cut tobacco, being cut lamina and/or cut stem tobacco. Alternatively, or in addition, the tobacco may be one or more of whole leaf tobacco, tobacco dust and reconstituted tobacco.

If deemed appropriate, the tobacco treated in accordance with the process of the present invention may be subjected to a conditioning step, whereby the moisture content of the tobacco, post-treatment, is brought to less than about 15%, preferably less than 13%.

When it is the case that following treatment of tobacco with the supercritical fluid, the nitrosamines are separated from the supercritical fluid extraction medium by subjecting the medium to a nitrosamine removal process, preferably the medium flows around a closed system.

Suitably, the closed system may comprise a first chamber, for the treatment of the tobacco with supercritical fluid, and a second chamber in which the nitrosamine removal process takes place, wherein the first and second chambers are interconnected by interconnecting means, pipe(s) for example. Such system further comprises fluid transfer means operable to cause the extraction medium to flow around the closed system. A nitrosamine removal material such as an ion-exchange resin



or adsorbent may reside in the second chamber, such that supercritical fluid extraction medium, following treatment of the tobacco therewith, is transferred via the interconnecting means to the second chamber, wherein nitrosamines are totally or substantially removed. The supercritical fluid extraction medium, minus nitrosamines, may then be returned to the tobacco in the first chamber.

Suitably, a plurality of interconnected chambers may be provided for the treatment of the tobacco with supercritical fluid and/or a plurality of interconnected chambers may be provided for the nitrosamine removal process. When it is the case that more than one chamber is provided for either the treatment of the tobacco or the nitrosamine removal process, or for both, the supercritical fluid may flow sequentially through the chambers.

Alternatively, the closed system may comprise a first or single chamber having inlet and outlet means wherein interconnecting means interconnect the inlet with the outlet means of the chamber. Suitably, the interconnecting means may serve for the transfer of supercritical fluid extraction medium, under the action of fluid transfer means, from the outlet means of the chamber to and through a nitrosamine removal process station to the inlet means of the chamber. Preferably, the amount of fluid in the interconnecting means is kept to a minimum. A nitrosamine removal material, such as

an ion exchanger or an adsorbent, may be contained within any suitable permeable container so as to provide a means by which fluid may pass through the container and a means by which the tobacco is prevented from contact with the nitrosamine removal material.

Alternatively the nitrosamine removal process may, for instance, be constituted by the transfer of the medium through a UV light source. In this instance, the interconnecting means must be pervious to UV light.

Suitably, a plurality of interconnected chambers may be provided for the treatment of the tobacco with supercritical fluid.

In addition to subjecting the tobacco to treatment with the supercritical fluid to extract nitrosamines from the tobacco, the tobacco may be subjected to a microbial deactivation process. As stated above microbes, including *Enterobacter agglomerans*, *Bacillus* spp, *Fusarium equiseti*, *Cladosporium cladosporoides*, *Altenaria alternata* and *Acremonium arxii* are thought to be responsible for or contribute to the production of nitrosamines during curing of the tobacco. In fact, it is thought that microbes may also be a contributory factor in the production of nitrosamines in tobacco during storage of cured tobacco. Thus a reduction in microbial activity in the tobacco by way of the microbial deactivation process reduces the likelihood of reformation of

nitrosamines in the tobacco post-extraction thereof. The microbial deactivation process may be carried out before or after subjecting the tobacco to the treatment with the supercritical fluid. A further alternative is to subject the tobacco to treatment with the supercritical fluid under microbial deactivating conditions, such that microbial deactivation and extraction occur simultaneously.

Suitably, the microbial deactivation process may comprise a pasteurisation process, wherein the tobacco is heated to a specified temperature and maintained at that temperature for a set period of time. By way of example, the tobacco may be heated to a temperature in the range of about 70° to about 150° Celsius for a period of between about 30 seconds to about 2 minutes. The heating may be effected by, for example, convection heating by way of contacting the tobacco with a gaseous heating medium, microwave heating or radio frequency heating.

Suitably, the moisture content of the tobacco being subjected to the sterilisation process is adjustable by way of either a pre- or a post-conditioning step.

Alternatively, the treatment of tobacco with, for example, ionising radiation, UV radiation, freeze drying or an electron beam to kill microbes may be used as the microbial deactivation process.

In addition to the treatment of the tobacco with the supercritical fluid to extract nitrosamines from the tobacco, the tobacco may also be subjected to a nitrite/nitrate removal process. Nitrites are important precursors of nitrosamines, whereas nitrates are precursors of nitrites. It is thought that following nitrosamine removal residual nitrites in the tobacco may be free to react with alkaloids also present in the tobacco thus to re-form nitrosamines. The nitrite/nitrate removal process may suitably comprise the steps of solvent extraction to remove the nitrites/nitrates from the tobacco, followed by ion exchange to bind the nitrites/nitrates. Alternatively, the nitrites may be removed by way of an oxidation step. In a yet further alternative, removal of nitrites/nitrates using micro-organisms as disclosed in any one of GB 1 440 171, GB 1 585 024, US 4709,710 or GB 2 014 031 may be used.

As with the microbial deactivation process, the nitrite/nitrate removal process may be carried out before, after or during the treatment of the tobacco with the supercritical fluid. When the nitrite/nitrate removal process is carried out simultaneously with the treatment of the tobacco with the supercritical fluid, the process may in order to remove nitrites from the tobacco comprise, for example, the step of either applying ascorbic acid to the tobacco prior to treatment of the tobacco with the supercritical fluid;

incorporating ascorbic acid with the supercritical fluid; or, when an ion exchanger or adsorbent material is present, incorporating ascorbic acid with the ion exchanger or adsorbent. The ascorbic acid has the effect of scavenging nitrites from the tobacco.

The nitrite/nitrate removal process may be carried out as an alternative to or in addition to the microbial deactivation process.

The inventive process provides a Burley tobacco having an initial nitrosamine content after curing in the range of about 0.3 ppm - about 30 ppm, which after processing has a nitrosamine content that is at least 45% lower. If the tobacco is a Burley tobacco having a nitrosamine content of 5-6 ppm, after processing the content is preferably 3.6 ppm or less.

The inventive process also provides a Virginia tobacco having an initial moisture content after curing of less than 8.5 ppm, which after processing has a nitrosamine content that is at least 45% lower.

Preferably the Burley or Virginia processed tobacco have a nitrosamine content of at least 60% lower than its original content.

The inventive process also provides a US blended tobacco having an original nicotine content in the range of 0.10 - 2.0% and a nitrosamine content in the range of 0.10 - 1.2 $\mu$ g/g

which after processing has a percentage decrease in nitrosamines to percentage decrease in nicotine in the range of 1:1 to 10:1.

The inventive process also provides a Virginia blended tobacco having an original nicotine content in the range of 0.30 - 2.15% and a nitrosamine content in the range of 0.10 - 1.5  $\mu\text{g/g}$ , which after processing has a percentage decrease in nitrosamines to percentage decrease in nicotine in the range of 1:1 to 10:1.

Preferably the ratio is in the range of 5:1 or more, and more preferably 8:1 or more.

In order that the present invention may be clearly understood and readily carried into effect reference will now be made, by way of example, to the accompanying diagrammatic drawing, in which:-

Figure 1 shows an apparatus for carrying out a process according to a first aspect of the present invention; and

Figure 2 shows an apparatus for carrying out a process according to an alternative aspect of the present invention.

The apparatus as shown in Figure 1 is a closed system comprising a first chamber 1 and a second chamber 2 wherein the first and second chambers 1, 2 are interconnected by interconnecting pipes 3. The closed system further comprises fluid transfer means, namely a pump 4. The apparatus further comprises a reservoir tank 5 interconnected

with the first chamber 1 via a duct 6. Valve 7 is located in duct 6 which valve 7 is operable to close the tank 5.

#### EXAMPLE 1

In operation of the Figure 1 apparatus, about 30kg of cut tobacco having a moisture content of either about 14% or 25% (see Table 1) is placed in the first chamber 1, the chamber having a volume of 150l. An ion exchanger, namely an acidic ion exchange resin (as available from Bayer GmbH) having a weight of 4.4kg, is placed into the second chamber 2, the chamber having a volume of 150l. The ion exchanger is mixed with about 500g of solid potassium citrate granules. The reservoir tank 5 is charged with carbon dioxide, which carbon dioxide is then pressurised by pump means (not shown) and is transferred by the pump means from the reservoir tank 5 to the first and second chambers 1, 2 and the interconnecting pipes 3 until the requisite extraction conditions are achieved, namely a pressure of about 250 bar and a temperature of about 70° Celsius. At this point the carbon dioxide reservoir tank is closed by closing valve 7. The supercritical carbon dioxide is then circulated, under the action of the pump 4, through the first chamber 1 (and, therefore, through the tobacco contained therein) and through the second chamber 2 (and, therefore, through the ion exchange resin therein) via the interconnecting pipes 3. The supercritical carbon dioxide extraction medium is circulated about the closed system for a

period of either 1.5 hours or 3 hours. Then the first and second chambers 1, 2 are decompressed by opening vent means (not shown) and the chambers are opened.

The nicotine and nitrosamine contents of the thus treated tobacco are then evaluated using suitable standard laboratory tests.

Such a tobacco extraction process has been found to remove a substantial proportion of tobacco specific nitrosamines from the treated tobacco. Table 1 discloses percentage reductions in the tobacco of both nicotine and nitrosamines following treatment of the tobacco as outlined above. The total amount of CO<sub>2</sub> used for these examples was 2190kg.

Table 1

Run No.	Tobacco m.c.	Extraction Period (h)	Nicotine Reduction (%)	Nitrosamines Reduction (%)
1	14%	1.5	67	90
2	14%	3.0	78.5	94
3	25%	1.5	65.5	93.5
4	25%	3.0	77	95



Treatment for 1.5 hours results in a greater difference between the percentage amount of nitrosamines and the percentage amount of nicotine extracted, as compared with treatment for 3 hours.

#### Example 2

It was believed that the extraction period outlined above could be reduced further without substantially affecting the percentage reduction of nitrosamines, whilst further reducing the percentage reduction of nicotine. For instance, the extraction period may be between about 15 minutes to about 1.5 hours, preferably between about 20 minutes to about 1 hour, more preferably between about 25 minutes to about 40 minutes and even more preferably about 30 minutes.

The conditions of extraction are preferably further biased towards the extraction in the supercritical fluid of nitrosamines, as compared with other tobacco specific compounds, such as nicotine. Several other methods of biasing the extraction towards nitrosamine removal, as compared with other tobacco specific compounds, may be used in addition to or separately from adjustment of the extraction period. For instance, the pH of the tobacco may be maintained at less than about 6.5, preferably about 5.5. In accordance with a further alternative, the supercritical fluid extraction medium may be saturated, or substantially saturated, with tobacco specific compounds, or commercially available chemical analogues

thereof, other than nitrosamines before contacting the extraction medium with the tobacco treatment. A yet further alternative, when the supercritical fluid is carbon dioxide, may be to cool the tobacco to a temperature below about 35°C, such that when the supercritical carbon dioxide is pumped into the chamber containing the tobacco the general effectiveness of the extraction process is reduced with preferential bias against the removal of tobacco specific compounds other than nitrosamines. Biasing towards the extraction of nitrosamines may also be effected by altering (i.e. increasing) the packing density of the tobacco in the extraction chamber.

Furthermore, biasing may be effected by altering, i.e. lowering the mass flow rate of the supercritical fluid extraction medium per unit mass of tobacco. For example, reducing the flow rate of the supercritical fluid per kg of tobacco to less than 30 kg/h. Each of the above outlined methods of biasing the extraction towards nitrosamine removal, as compared with other tobacco specific compounds, may be carried out separately or in various combinations with one another.

As an optional addition to the above described process, the ion exchange resin situate in the second chamber 2, following decompression of the closed system, is flushed or washed with water. The washings are then treated with UV light from a UV light source (not shown). Exposure of the

washings to UV light results in the degradation of nitrosamines in the washings. Extract(s) other than nitrosamines in the washings is then re-incorporated with the tobacco. Other extract(s) may include, for example, nicotine and/or flavour substances. In this way, the end result is that nitrosamines are selectively removed from the tobacco, without adversely affecting the taste of the tobacco.

Some examples of the above described variations are disclosed in Table 2 below.

In view of the variability of nicotine and nitrosamine contents in each batch of tobacco, 300g from each batch was retained as a control for the batch. The nicotine and nitrosamine levels for each control from the 4 batches sampled are given in Table 3 below.

Table 2

Trial / run	Tob type & wt	Nicotine in blend %	% nicotine reduction	Total TSNA in blend $\mu\text{g/g}$	% TSNA reduction	Extraction time	Total $\text{CO}_2\text{kg}$	Other process variables
1 run 2	238 / 35kg	0.53	78.46	0.14	94.33	3 hrs	2190	15% moist tobacco
1 run 4	238 / 35 kg	0.56	77.24	0.12	95.14	3 hrs	2190	25 % moist tobacco
1 run 5	238 / 35 kg	0.33	86.59	0.15	93.93	3 hrs	2190	500g Citrate added to ion exchanger
1 run 7	USB / 35kg	0.17	91.58	0.12	97.12	3 hrs	2190	15% moist tobacco
1 run 9	USB / 35kg	0.14	93.07	0.20	95.20	3 hrs	2190	25% moist tobacco
4 run 1	USB/3kg	1.47	20.11	1.13	61.69	2hrs	40	At original pH (5.44)
4 run 3	USB / 3 kg	1.7	7.61	1.08	63.39	2 hrs	40	pH of tobacco reduced (4.1-4.3)
4 run 4	238 / 3 kg	1.96	14.78	0.72	70.49	2 hrs	40	
4 run 6	238 / 3 kg	2.12	7.83	1.36	44.26	2 hrs	10	
3 run 11	238 / 15 kg	2.1	8.7	0.65	73.36	15 mins	200	
5 run 3	USB / 3 kg	1.4	22.65	1.11	66.57	2.5 hrs	40	Glass beads, no ion exchanger

TABLE 3

Batch No.	Nicotine Content (%)		Nitrosamine Content ( $\mu\text{g/g}$ )	
	USB	238	USB	238
1	2.02	2.46	4.17	2.47
4	1.84	2.30	2.95	2.44
3	1.84	2.29	2.95	2.44
5	1.77	not reported yet	3.32	not reported yet

EXAMPLE 3

The apparatus shown in Figure 2 is also a closed system, which apparatus comprises a chamber 1 provided with an inlet 8 and an outlet 9, interconnecting pipe 10, wherein the pipe 10 interconnects the inlet 8 with the outlet 9 of the chamber 1, and fluid transfer means, i.e. a pump 4. This apparatus further comprises a reservoir tank 5 interconnected with the chamber 1 via a duct 6. Valve 7 located in duct 6 allows for tank 5 to be closed. Adjacent a position of the pipe 10 is located a UV light source.

In operation of the Figure 2 apparatus about 100kg of cut tobacco having an appropriate moisture content is placed into chamber 1. The reservoir tank 5 is charged with carbon dioxide, which carbon dioxide is then pressurised by pump means (not shown) and is transferred by the pump means from

the reservoir tank 5 to the chamber 1 and pipe 10 until the requisite extraction conditions are achieved, namely a pressure of about 250 bar and a temperature of about 50° Celsius. Then the tank 5 is closed by closing the valve 6. The supercritical carbon dioxide is then circulated, under the action of the pump 4, through the chamber 1 (and, therefore, through the tobacco contained therein) and through the pipe 10. The UV light source 11 irradiates the supercritical carbon dioxide extraction medium in the pipe 10. Thus, nitrosamines in the supercritical carbon dioxide are degraded. Degradation products thereof may then be removed, for instance by passing the supercritical carbon dioxide through a metal mesh (not shown). The pipe 10 is comprised of, at least in the region of the UV light source 11, material which is pervious to UV light, e.g. a high pressure quartz window. The amount of supercritical carbon dioxide in the interconnecting pipe 10 is kept to a minimum by use of a pipe 10 having a bore of a small diameter (i.e. a diameter of about 1cm). The supercritical carbon dioxide is, following exposure to the UV light, returned to the chamber 1 and again into contact with the tobacco therein. The supercritical carbon dioxide is circulated for a period of 30 minutes. Then the chamber 1 and the pipe 10 are decompressed by opening vent means (not shown). The tobacco treated in this way is free, or substantially free, of nitrosamines, whilst the nicotine

content of the tobacco remained substantially the same pre- and post-treatment.

A further alternative apparatus (not shown) comprises substantially the apparatus shown in Figure 2 with a nitrosamine removal material held within a fluid permeable container in the chamber 1. The fluid may be re-circulated through the system for a number of times before removal and optional subsequent removal of nitrosamines therefrom.

CLAIMS

1. A tobacco treatment process wherein tobacco is subjected to treatment with a supercritical fluid extraction medium to extract nitrosamines from said tobacco.
2. A process according to Claim 1, whereby said nitrosamines are separated from said supercritical fluid extraction medium by subjecting said extraction medium to a nitrosamine removal process.
3. A process according to Claim 2, wherein said nitrosamine removal process comprises a chemisorption step.
4. A process according to Claim 3, wherein said chemisorption step comprises the use of an ion exchanger.
5. A process according to Claim 2, wherein said nitrosamine removal process comprises an adsorbent step.
6. A process according to Claim 5, wherein an adsorbent of said adsorbent step is selected from one or more of the group consisting of glass beads, activated charcoal, aluminium silicate and zeolites.
7. A process according to Claim 2, wherein said nitrosamine removal process comprises treatment of said extraction medium with ultraviolet (UV) light.
8. A process according to Claim 2, wherein said nitrosamine removal process comprises either precipitation of said nitrosamines from said extraction medium, or subjecting



said extraction medium to nitrosamine-specific enzyme breakdown, or chromatographic separation of said nitrosamines from said extraction medium.

9. A process according to any one of Claims 2-8, wherein said nitrosamine removal process comprises a plurality of removal processes.
10. A process according to any one of Claims 2-9, wherein following said nitrosamine removal process, said extraction medium, being wholly or substantially free of said nitrosamines, is brought into contact with the tobacco, such that extract(s) other than nitrosamines in said extraction medium may be incorporated or re-incorporated with said tobacco.
11. A process according to Claim 10, wherein said extract(s) comprise nicotine and/or flavour substances.
12. A process according to any one of the preceding claims wherein said supercritical fluid extraction medium is supercritical carbon dioxide.
13. A process according to any one of the preceding claims, wherein an acid is added to said tobacco prior to treatment of said tobacco with said supercritical fluid; or to said supercritical fluid prior to treatment of said tobacco with said supercritical fluid.

14. A process according to any one of Claims 4 or 5 when appended to Claim 3, wherein an acid is added to the ion exchanger or adsorbent.
15. A process according to any one of Claims 1-14, wherein one or more of an organic solvent or an alcohol is added in addition to, or alternatively of, said acid.
16. A process according to Claim 15, wherein said acid is an organic acid.
17. A process according to Claim 16, wherein said acid is an organic acid selected from one or more of the group consisting of malonic acid, ascorbic acid, succinic acid, glutamic acid, adipic acid, malic acid, tartaric acid, mucic acid and citric acid, or a salt derivative thereof.
18. A process according to Claim 17, wherein said organic acid is a citric acid salt.
19. A process according to Claim 18, wherein said citric acid salt is potassium citrate.
20. A process according to any one of the preceding claims, wherein said extraction of said nitrosamines from said tobacco with said supercritical fluid takes place at an elevated pressure and temperature.
21. A process according to Claim 20, wherein when supercritical fluid is supercritical carbon dioxide, said pressure is in the range of 100 to 350 bar.

22. A process according to Claim 21, wherein said pressure is about 200 to 300 bar.
23. A process according to Claim 22, wherein said pressure is about 240 to 260 bar.
24. A process according to any one of Claims 20-23, wherein said temperature is greater than about 35°Celsius.
25. A process according to Claim 24, wherein said temperature is in a range of about 35° to about 140° Celsius.
26. A process according to Claim 25, wherein said temperature is in a range of about 35° to about 90° Celsius.
27. A process according to any one of the preceding claims, wherein said tobacco is placed in a closable chamber or bomb during said extraction treatment thereof with supercritical fluid.
28. A process according to any one of Claims 20 to 27, wherein said elevated temperature is effected by heat transfer or by electromagnetic radiation.
29. A process according to any one of the preceding claims wherein no, or very little, nicotine is removed from said tobacco in said extraction medium.
30. A process according to any one of the preceding claims, wherein the pH of said tobacco is less than about 6.5.
31. A process according to Claim 30, wherein said pH of said acid is less than about 5.5.

32. A process according to any one of the preceding claims, wherein the ratio of the percentage reduction in nitrosamines to the percentage reduction in nicotine is in the range of about 1.1:1 to about 18:1.
33. A process according to Claim 32, wherein said ratio is in the range of about 1.3:1 to about 10:1.
34. A process according to Claim 33, wherein said ratio is in the range of about 2:1 to about 6:1.
35. A process according to any one of the preceding claims, wherein a suitable mass flow rate of said supercritical fluid extraction medium per kg of tobacco is about 1-55kg/h.
36. A process according to Claim 35, wherein said mass flow rate is in the range of 10-40 kg/hr.
37. A process according to Claim 36, wherein said mass flow rate is in the range of 15-35 kg/hr.
38. A process according to Claim 37, wherein said mass flow rate is about 30 kg/h.
39. A process according to any one of the preceding claims, wherein said tobacco treated in accordance with said process is cut tobacco and/or whole leaf tobacco, tobacco dust or reconstituted tobacco.
40. A process according to any one of the preceding claims, wherein said tobacco is subjected to a microbial deactivation process.

41. A process according to Claim 40, wherein said microbial deactivation process comprises a pasteurisation process.
42. A process according to Claim 41, wherein said tobacco is heated to a temperature in the range of about 70°C to about 150°C for a period of between 30 seconds to 2 minutes.
43. A process according to Claim 41, wherein said pasteurisation process is effected by heating of said tobacco by convection heating by way of contacting said tobacco with a gaseous heating medium, by microwave heating or by radio frequency heating.
44. A process according to any one of Claims 40-43, wherein the moisture content of said tobacco being subjected to said microbial deactivation process is adjustable by way of either a pre- or post- conditioning step.
45. A process according to Claim 41, wherein said microbial deactivation process comprises use of ionising radiation, UV radiation, freeze drying or an electron beam.
46. A process according to any one of Claims 1-45, wherein said tobacco is subjected to nitrite/nitrate removal process, before, during or after treatment of said tobacco with said supercritical fluid.
47. A process according to Claim 46, wherein said nitrite/nitrate removal process comprises the steps of solvent

extraction to remove nitrites/nitrates from said tobacco followed by ion exchange to bind said nitrites/nitrates.

48. A process according to Claim 46, wherein said nitrite removal process comprises an oxidation step or use of micro-organisms.

49. A process according to any one of Claims 46-48, wherein ascorbic acid is applied to said tobacco, incorporated with said supercritical fluid, or incorporated with a chemisorption medium.

50. A nitrosamine extraction apparatus in use according to any one of the preceding claims, said apparatus being a closed system comprising a first chamber for the treatment of said tobacco with supercritical fluid, a second chamber in which said nitrosamine removal process takes place, said chambers being interconnected by interconnecting means, said apparatus further comprising supercritical fluid supply means supplying supercritical fluid, fluid transfer means operable to cause said supercritical fluid to flow around said closed system, and a nitrosamine removal material residing in said second chamber.

51. Apparatus according to Claim 50, wherein said fluid transfer means is a pump.

52. Apparatus according to Claim 50, wherein said fluid transfer means is a pressure differential system.

53. Apparatus according to any one of Claims 50-52, wherein a plurality of interconnected chambers are provided for said treatment of said tobacco with supercritical fluid and/or a plurality of interconnected chambers are provided for said nitrosamine removal process.
54. Apparatus according to Claim 53, wherein said supercritical fluid flows sequentially through said chambers.
55. A nitrosamine extraction apparatus in use according to any one of Claims 1-49, said apparatus being a closed system, wherein said closed system comprises a chamber having inlet and outlet means connected by interconnecting means, fluid transfer means and nitrosamine removal means.
56. Apparatus according to Claim 55, wherein said nitrosamine removal means comprises an ion exchanger or an adsorbent held in a supercritical fluid permeable container within said chamber.
57. A closed system according to Claim 56, wherein said interconnecting means serve for the transfer of supercritical fluid extraction medium under the action of fluid transfer means, from said outlet means of said chamber and through a nitrosamine removal process station to said inlet means of said chamber.

58. A Burley tobacco having an initial nitrosamine content after curing in the range of about 0.3 ppm - about 30 ppm, wherein said Burley tobacco has a nitrosamine content that is at least 45% lower following treatment according to the process of any one of Claims 1-49.
59. A Virginia tobacco having an initial nitrosamine content after curing less than 8.5 ppm, wherein said Virginia tobacco has a nitrosamine content that is at least 45% lower following treatment according to the process of any one of Claims 1-49.
60. A Burley or Virginia tobacco according to Claim 59 or 60, wherein said nitrosamine content is at least 60% lower than the original content.
61. A Burley tobacco having an initial nitrosamine content of 5-6 ppm, the nitrosamine content after treatment according to any one of Claims 1-49 being 3.6 ppm or less.
62. A US blended tobacco having an original nicotine content in the range of 0.10 - 2.0% and a nitrosamine content in the range of 0.10 - 0.12  $\mu\text{g/g}$ , wherein said blend after processing according to any one of Claims 1-49 has a ratio of percentage decrease in nitrosamines to percentage decrease in nicotine in the range of 1:1 to 10:1.



63. A Virginia tobacco blend having an original nicotine content in the range of 0.10 - 2.0% and a nitrosamine content in the range of 0.10 - 1.2  $\mu\text{g/g}$ , wherein said blend after processing according to any one of Claims 1-49 has a ratio of percentage decrease in nitrosamine to percentage decrease in nicotine in the range of 1:1 to 10:1.
64. A tobacco blend according to Claim 62 or 63, wherein said ratio is preferably 5:1 or more.
65. A tobacco blend according to Claim 62 or 63, wherein said ratio is preferably 8:1 or more.
66. A tobacco treatment process substantially as hereinabove described with reference to Figures 1 and 2 hereof.

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Fig.1.

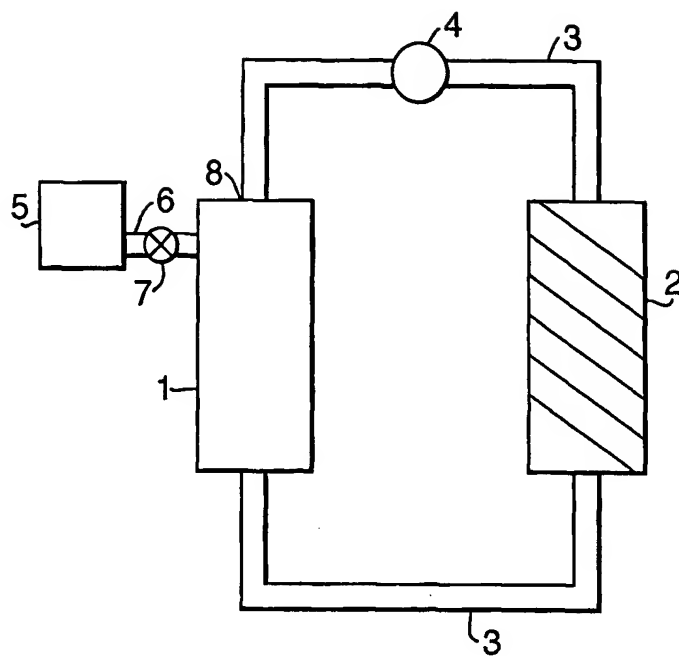
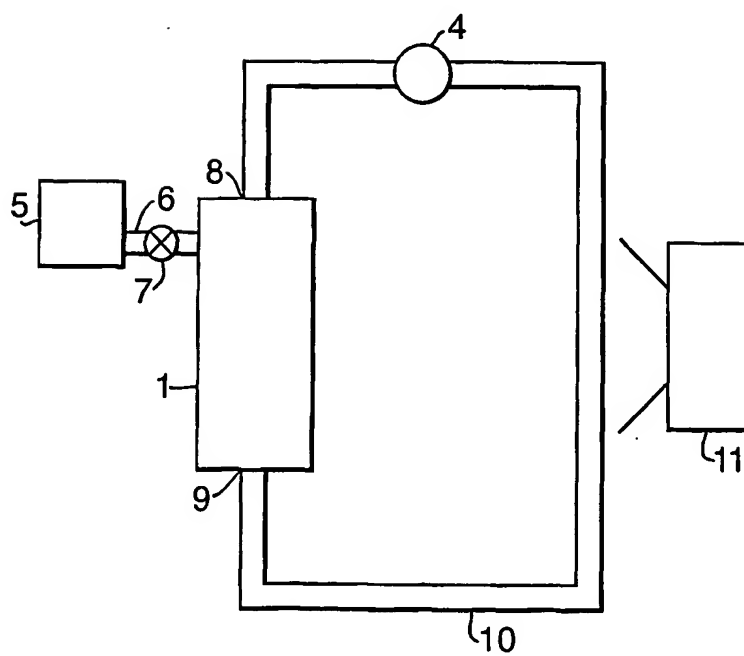


Fig.2.



## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 01/00945

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 A24B15/24 A24B15/26

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A24B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, FSTA, COMPENDEX

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 5 810 020 A (SALTER ROBERT ET AL) 22 September 1998 (1998-09-22)	1-4, 10-12, 15, 27, 30, 39, 40, 46, 47, 50-57
Y	the whole document	41, 43, 44
X	WO 98 05226 A (WILLIAMS JONNIE R) 12 February 1998 (1998-02-12) claims 18-63; tables 1-11	58-66
Y		41, 43, 44
A	US 4 153 063 A (ROSELIUS WILHELM ET AL) 8 May 1979 (1979-05-08) abstract	50-57
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☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

3 July 2001

Date of mailing of the international search report

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